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THE ELECTRICAL CONDUCTIVITY OF SOLID OXIDE SYSTEMS.

II. THE SYSTEM $\text{ZrO}_2\text{-CaO}$.

ELECTRICAL CONDUCTIVITY AND TRANSPORT NUMBERS

By

Z. S. Volchenkova and S. F. Pal'guyev

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By: Z. S. Volchenkova and S. F. Pal'guyev

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PREPARED BY:

TRANSLATION SERVICES BRANCH
FOREIGN TECHNOLOGY DIVISION
WP-AFB, OHIO.

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THE ELECTRICAL CONDUCTIVITY OF SOLID OXIDE SYSTEMS. II
THE SYSTEMS ZrO_2 -CaO. ELECTRICAL CON-
DUCTIVITY AND TRANSPORT NUMBERS

Z. S. Volchenkova and S. F. Pal'guyev

Measurements of the electrical conductivity of the solid-oxide system ZrO_2 - CaO, judging by the data in the literature [1,2,3], have been carried out only for certain compositions and do not cover a number of temperature ranges.

It is interesting to measure electrical conductivities over a broad range of compositions and temperatures and also to verify by direct measurements (by determination of the transport numbers) statements occurring in the literature to the effect that solid solutions of the oxides ZrO_2 - CaO, containing 10-20 mole % calcium oxide, are purely ionic conductors [4].

Therefore we have investigated the temperature dependences of the electrical conductivity of solid samples over a range of compositions from pure zirconium dioxide to pure calcium oxide in the range of temperatures from 300 to 1000°. The transport numbers of samples of a number of compositions were studied. In addition, the structural characteristics of sintered samples were examined, as well as some of

their ceramic properties.

Experimental Portion

Preparation of samples. We took zirconium dioxide (impurity content no more than: 0.01% magnesium, 0.001% silicon and manganese, 0.0001% copper and yttrium) and calcium oxide (anal. grade) or calcium carbonate (cp).

The oxides were first roasted at a temperature of 1200° for two hours. When the samples contained up to 40 mole % calcium oxide, the oxide was taken for their preparation; in the case of higher contents of calcium oxide an appropriate amount of the carbonate was taken instead of the oxide.

The initial components of the mixture were milled and screened through a 200 mesh sieve. The mixtures of oxides weighed out according to calculation were prepared by extremely thorough pulverization in an agate mortar. The samples were molded in the form of tablets with the dimensions 1.0 X 1.0 X 0.2 - 0.4 cm under a pressure of about 4000 kg/cm². The sintering was carried out at 1500° ± 20° with a holding of one hour at the maximum temperature.

We determined the linear shrinkage of the samples during sintering, as well as their quality and color.

The sintered samples underwent an x-ray diffraction analysis. RKD powder chambers were used in the presence of K_α copper radiation. The x-ray measurements were performed by G. V. Burov, for which the authors thank him.

Investigation of the structure and ceramic properties. The results of the investigation of the structural components and the ceramic properties of the solid-oxide system ZrO₂ - CaO are summarized in Table 1.

As follows from the table, solid solutions with a fluorite type crystal lattice are formed in the system ZrO_2 - CaO at 1500° , as soon as the calcium-oxide content reaches 10 mole %. According to the data of American authors [5], even at 2000° , solid solutions are formed in the system we are investigating, only when the calcium-oxide content is not less than 16 mole %. According to the results of our research, the range of solid solutions is wider in this case with respect to the scale of compositions and also includes solutions containing 40 mole % calcium oxide (as opposed to 35 mole % CaO according to [5]). This agrees with the results of an earlier paper [6].

In the range of the primary solid solution (10-40 mole % calcium oxide) very good ceramics are obtained. The density and hardness of samples having these compositions was extremely high. They were capable of being preserved in air for a long period of time.

Samples containing 80 - 90 mole % calcium oxide were of approximately the same quality immediately after sintering. However, during storage they rapidly decomposed, thus attesting to the presence of calcium oxide in them; this calcium oxide reacted with the moist air to form the hydroxide.

According to our own data and that of the literature [6,7], the chemical compound CaZrO_2 is formed in the ZrO_2 - CaO system in the case of a composition consisting of 1 mole of calcium oxide to 1 mole of zirconium oxide. The formation of calcium zirconate is accompanied by an increase in the porosity and volume of the samples [7,8], which reduces their shrinkage considerably.

Actually, in our case the samples similar in composition to calcium zirconate (No. 7 and 8) have the least shrinkage and are bad ceramics. The ceramic properties of the samples improve somewhat with

an increase in their calcium-oxide content. However, as already noted above, they decompose rapidly during storage.

Table 1

Phase Components and Certain Ceramic Properties of Sintered Solid Oxides of the ZrO_2 - CaO System.

Sample No.	Composition, mole %		Phase composition and crystal lattice parameters a, k X	% linear shrinkage	Color	Sinter-ability
	ZrO_2	CaO				
1	100	0.00	Monoclinic	13.0	White	—
2	90.0	10.0	CaF_2 type lattice, $a=5.116 \pm 0.002$	15.0	White	Good
3	85.0	15.0	CaF_2 type lattice, $a=5.121 \pm 0.002$	16.0	White	Good
4	80.0	20.0	CaF_2 type lattice, $a=5.126 \pm 0.002$	15.8	White	Good
5	70.0	30.0	CaF_2 type lattice, $a=5.132 \pm 0.002$ + weak CaZrO_3 lines	12.1	White	Good
6	60.0	40.0	CaF_2 type lattice, $a=5.142 \pm 0.003$ + CaZrO_3 lines	8.8	White	Satisfactory
7	50.0	50.0	CaZrO_3	3.8	Bright-rose	Very Bad (friable)
8	40.0	60.0	CaZrO_3 + (CaO)	3.0-3.4	Rose	Very Bad (friable)
9	33.0	67.0	CaZrO_3 + (CaO)	7.35	Soft-rose	Bad
10	30.0	70.0	CaZrO_3 + CaO	8.7-11.1	Faint-rose	Satisfactory
11	20.0	80.0	CaZrO_3 + CaO	15.7	Almost white	Very good
12	10.0	90.0	CaO + CaZrO_3	18.1	White	Very good
13	0.00	100.0	CaO + weak $\text{Ca}(\text{OH})_2$ lines	25.0	White	Good

Note. The CaZrO_3 and CaO lattice parameters do not vary within the limits of the measurement errors.

The conductivity measurements were carried out by the contact method with the aid of an a-c bridge. This method is described in detail in two of our papers [9-10]. The accuracy of the measurements was of the order of 1.0% of the measured resistance.

The temperature dependence of the conductivity in the range from 300-1000° was measured for all compositions. The measurements were carried out while the temperature was being raised and also while it

was being lowered. The results were in good agreement.

The logarithms of the values obtained for the conductivity were plotted against the reciprocal of the absolute temperature. The temperature dependence of the conductivity was thus obtained in the form of a straight line satisfactorily described by the equation

$$\kappa + Ae^{\frac{-\Delta E}{2kT}} \quad (1)$$

where κ is the conductivity; A and ΔE are constants; k is Boltzmann's constant; and T is the absolute temperature.

For all compositions except those in the range of formation of solid solutions the straight lines of the temperature dependence have a break, as a rule, at 750-800°.

In Fig. 1 the temperature dependences of the conductivity of samples of certain compositions are given for the purpose of illustration.

The following facts should be noted. The conductivity of samples containing more than 50 mole % calcium oxide, if they had been kept in air for some time, were considerably (about one order of magnitude) higher than the conductivity of the same samples measured immediately after they were roasted. At 700-800° the temperature-dependence curves of the electrical conductivities of samples that had been kept in air exhibited a sharp break, since the conductivity fell rapidly to the normal value. This situation is clearly visible in Fig. 2. When the measurements of the conductivities were repeated the very same values were obtained. Therefore all measurements of the conductivity of samples containing more than 50 mole % calcium oxide were made immediately after sintering, or, if they had been stored for some time, after additional roasting at 1000°.

It may be seen in Table 1 that lines of pure calcium oxide appear in the roentgenograms of samples containing more than 50 mole % calcium oxide. When stored in air (even for a relatively short time) this oxide on the surface of the samples reacts with moisture and carbon dioxide, forming the hydroxide and the carbonate (in the case of pure calcium oxide faint hydroxide lines were noticed on roentgenograms taken some time after the roasting). This increases the conductance of these samples. At 700-800° the compounds that have been formed begin to decompose, and this gives rise to a sharp decrease in the conductivity.

Conductivity isotherms for different temperatures and the curve of the variation in the conductivity activation energy ΔE for the high temperature range are shown in Fig. 3. The linear shrinkage during sintering of samples of various compositions is also given there for comparison with the above-mentioned quantities.

It can be seen in Fig. 3 that in the region of formation of solid solutions of zirconium and calcium oxide the conductivity increases rapidly. This rise in conductivity accompanying an increase in the calcium-oxide content in the solid solution may be explained by the rapid increase in the number of oxygen vacancies in the solution's crystal lattice. In the case of small calcium-oxide contents the defects are distributed statistically. When the content of calcium oxide in the solid solution is increased further, the number of defects in the crystal lattice increases to such an extent that as a result of their interaction with one another they assume an ordered distribution. Because of this, certain difficulties arise to impede the motion of the oxygen ions among these vacancies, and the conductivity, having ceased to increase, begins to decrease. In this case the highest

conductivity is found for samples containing 15 mole % calcium oxide. Accordingly, it is for this composition that the minimum conductivity activation energy is observed.

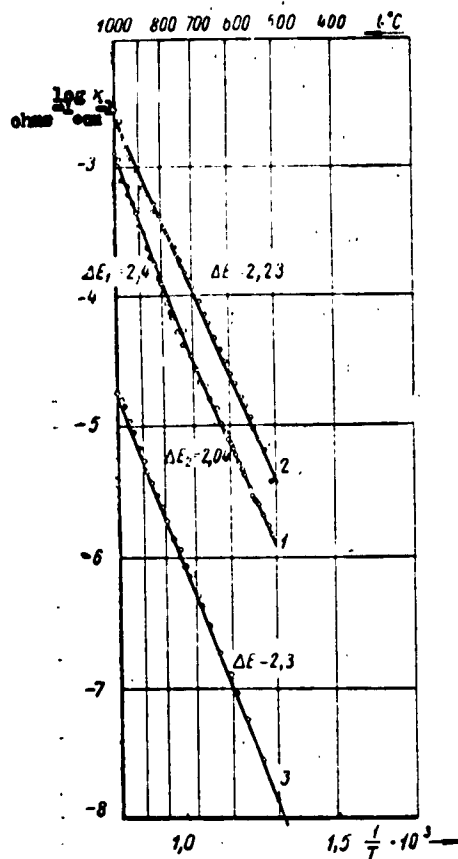


Fig. 1. Temperature dependence of conductivity: 1) 90 mole % zirconium dioxide and 10 mole % calcium oxide; 2) 85 mole % ZrO_2 and 15 mole % CaO ; 3) 60 mole % ZrO_2 and 40 mole % CaO .

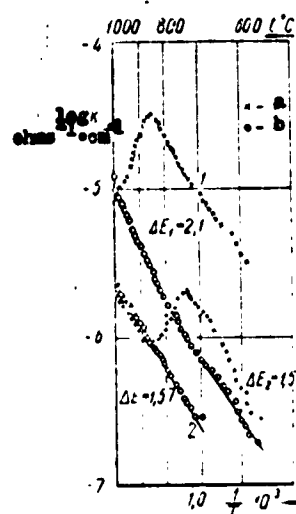


Fig. 2. Temperature dependence of conductivity: 1) 30 mole % ZrO_2 and 70 mole % calcium oxide; 2) pure CaO ; a) first measurement b) second measurement.

It is interesting that with an increase in the number of vacancies the percentage of linear shrinkage increases somewhat, instead of decreasing, as was the case with the $CeO_2 - ZrO_2$ system [11].

Here the different distribution of the defects in the crystal lattice may have had some influence. While in the formation of solid solutions in the CeO_2 - ZrO_2 system vacancies are most likely to arise at lattice points belonging to Ce^{4+} and O^{2-} [11], in ZrO_2 - CaO solid solutions vacancies are found only in the oxygen portion of the crystal lattice [1,2].

In the case of a composition consisting of 1 mole of zirconium dioxide to 1 mole of calcium oxide calcium zirconate is formed. This fact is reflected in the conductivity; the minimum conductivity and, correspondingly, the maximum activation energy is observed for this composition.

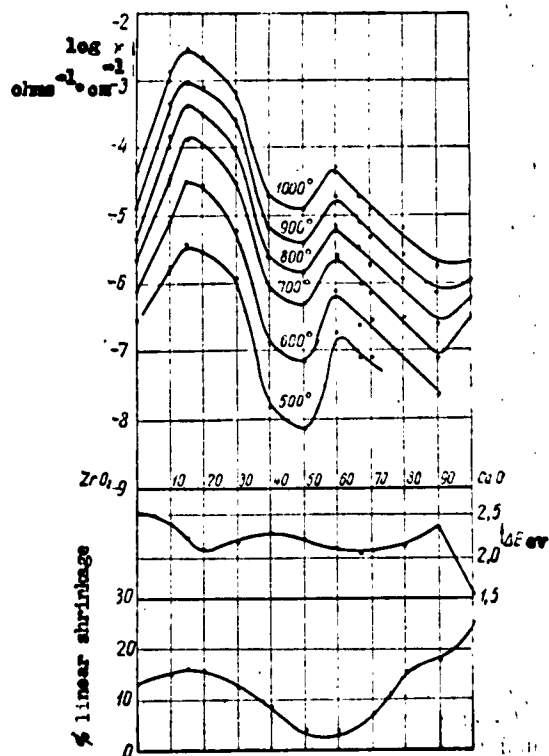


Fig. 3. Conductivity isotherms; variation of conductivity activation energy and linear shrinkage with composition for samples of the system ZrO_2 - CaO .

Subsequently, with an increase in the CaO content in the samples the conductivity increases; when the samples contain 60 mole % calcium oxide, a relatively small conductivity maximum and, correspondingly, an activation energy minimum occurs, probably as a result of the formation of a eutectic of a calcium zirconate and calcium oxide [3]. When the composition approaches that of pure calcium oxide, a drop in conductivity occurs. In the region of 90 mole % calcium oxide a small conductivity minimum is noted together with a corresponding small activation energy maximum, due, possibly, to the nonequilibrium nature of the samples.

In contrast to the results in Ref.[3], we found no conductivity minimum corresponding to the formation of the compound $2\text{ZrO}_2 \cdot \text{CaO}$. The formation of this compound is doubtful, since the results of the x-ray diffraction analysis give no indications of its existence.

The conductivity maxima and minima are not displaced along the composition axis during a change in temperature. In this respect the system which we are investigating is analogous to the cerium dioxide-zirconium dioxide system [10].

Measurements of transport numbers in oxide systems, which make it possible to judge the nature of the current carriers, are of very great interest. These measurements, however, are attended with considerable difficulties, the most important of which are the high temperatures, since at low temperatures the conductivities of the solid solutions, which are of interest to us, are insignificant. Even at operating temperatures (of the order of 1000°) their conductances are low. This latter state of affairs makes it necessary to carry out the electrolysis at low current densities and for a fairly long period of time. Under these conditions various secondary

processes, which would materially distort the results of the experiment, may occur.

We performed the measurements of the transport numbers by the weight method, which had been used earlier for similar purposes [10].

For the measurements we took three oxide plates 20 mm in diameter and 3-4 mm in thickness, which had been prepared in the usual way. They served as the electrolyte: two plates as the catholyte and anolyte and one as the middle partition. They were carefully polished to fit against one another, clamped between platinum electrodes in an apparatus described in one of our papers [9], and heated to 1000°. The electrolysis was then carried out. The electrolysis current was equal to 0.02 - 0.03 amp. A copper coulometer was connected into the circuit to measure the amount of electricity passing through. The electrolysis lasted 2-4 hrs.

After electrolysis areas were noticed on the cathode which differed in color from the rest of the surface. Dark spots were also visible on the electrolyte plate adjoining the cathode. No visible changes were noted either on the anode or the other plates. When the cathode plate and the cathode were roasted at 1000°, the dark areas lightened, and the plate assumed its initial appearance; its weight in this case increased somewhat.

The transport numbers were calculated according to the change in the weights of the anode and cathode electrolyte plates, which were weighed together with the electrodes. In all cases the weight of the middle plate did not change in the course of electrolysis.

The calculation of the transport numbers was done according to the formulas:

$$t_k = \frac{\Delta a \cdot 1.19}{A \cdot B}, \quad (2)$$

$$t_a = \frac{\Delta k \cdot 1.19}{A \cdot B}, \quad (3)$$

where t_c and t_a are the transport numbers of the cation and anion, respectively; Δa and Δc are the changes (decreases) in the weights of the anode and cathode electrolyte plates, respectively; A is the mean electrochemical equivalent of a solid solution of a given composition; B is the weight of the copper precipitated in the coulometer; 1.19 is the electrochemical equivalent of copper.

The oxygen evolved at the anode during electrolysis can be easily removed and does not affect the weight of the anode and the anolyte. Therefore, from the change in the weight of the anode plate we can immediately calculate the over-all transport number of the cations, i.e., the fraction of cation conductance.

The question of the cathode and the cathode electrolyte plate is more complicated. During electrolysis the metal precipitated at the cathode partially penetrates into the oxide electrolyte. Therefore the cathode and the catholyte are roasted after the experiment and according to their increase in weight a correction for the weight of the precipitated metal is calculated. In this case we assume that only zirconium ions are discharged at the cathode. It should be noted that this correction was relatively large, and an inaccuracy in its determination, which is quite possible, could distort the results considerably.

Measurements were made on samples of three compositions located in the solid-solution range of the oxide system under investigation. The results thus obtained are summarized in Table 2.

Table 2

Transport Numbers in the $\text{ZrO}_2\text{-CaO}$ System
at 1000°.

Composition	t_c (over-all)	t_a
0.9ZrO ₂ ·0.1CaO	0.001-0.009	0.02-0.06
0.8ZrO ₂ ·0.2CaO	0.001-0.01	0.03-0.04
0.6ZrO ₂ ·0.4CaO	0.001-0.004	0.08-0.14

Thus, according to the data obtained, in the system being investigated t_c is less than 0.01, while t_a is not more than 0.14, i.e., the ionic conductance amounts to only about 0.1 of the total conductance. But this causes doubt, since according to [4] and to measurements performed in our laboratory by means of the emf method [12], all of these compositions possess practically 100% ionic conductance. Therefore, our values for the transport numbers have been understated, more accurately, the anion transport number has been understated. This could have happened for a number of reasons.

First of all, the metal precipitated at the cathode may be dissolved in the oxide electrolyte, thereby giving rise to electronic conductance. The metal may be precipitated in the form of filaments (dendrites) and, by intergrowing the electrolyte, distort the results of the experiments. Oxidation of the metal precipitated at the cathode during electrolysis may also introduce a large error.

Since we carried out the electrolysis in air, there exists the possibility that, instead of metal being precipitated, oxygen was dissolved at the cathode according to the reaction:



If the current in the electrolyte is carried only by oxygen ions, then no weight changes will be observed in either the catholyte or the anolyte in this case. But if cations also participate in carrying the current, this will be manifested in a decrease in the weight of the anolyte and in a corresponding increase in the weight of the catholyte. When both reactions proceed jointly (ionization of the oxygen and discharge of the metal ions), the weight changes in the cathode electrolyte plate and the cathode will be more complicated.

When electronic conductance arises as a result of the dissolution in the oxide electrolyte of metal precipitating at the cathode, or when the electrolyte is intergrown by metallic dendrites, the measured transport numbers of the ions should depend on the duration of the electrolysis, viz., their value should decrease with an increase in the amount of electricity being passed through.

In order to establish whether or not this happens in our experiments, we have determined the transport numbers for different durations of the electrolysis. It was found that when the duration of the electrolysis was increased, all other conditions being equal, the transport numbers decreased all the more, the longer the electrolysis was continued. Therefore, the set of circumstances referred to distorted the results of our measurements. This is also indicated by observations of the variation of the voltage across the cell during electrolysis. Usually the voltage drop across the cell decreased rapidly soon after the beginning of the electrolysis. This decrease continued even further, but more slowly.

There were no complications of this type for the anolyte (oxygen does not dissolve in the electrolyte under investigation [4]). It is therefore very likely that the fraction of cation conductance found

by us is close to the true one.

In the future we propose to carry out a more detailed investigation, to clarify the extent to which the weight method is applicable in measuring transport numbers of oxide systems.

Since we know the fraction of cation conductance from the relationship $t_o + t_a = 1$, we can compute the anion transport number. But for this we must be positive that there is no electronic conductance. In the majority of cases this is not so. But in this case, as we have already said, there is no electronic conductance, and since the cation transport number is close to zero, the anion transport number should be close to unity.

Thus, solid solutions of calcium and zirconium oxides at 1000° are, for all practical purposes, purely anionic conductors. This fact allows us to use them as solid solutions in high-temperature fuel elements. However, the relatively low conductivity of the electrolyte does not allow us to obtain significant currents from it. Nevertheless, such an element can be used in a number of cases.

Conclusions

1. The structural components and ceramic properties of samples of different compositions of the zirconium dioxide-calcium oxide system have been investigated. It has been shown that in the range from 10 to 40 mole percent of calcium oxide at 1500° solid solutions possessing good ceramic properties are formed.

2. The temperature dependences of the conductivities of samples of different compositions of the ZrO_2 - CaO system have been measured, and the conductivity activation energies have been calculated. The highest conductivity is found for solid solutions containing

10-20 mole percent calcium oxide (conductivity of the order of $3 \cdot 10^{-3} \text{ ohms}^{-1} \cdot \text{cm}^{-1}$ at 1000°).

The conductivity isotherms and the variation in the conductivity activation energy with composition have extremums. This shape of the curves is caused by the crystal structure of the system of oxides being investigated.

3. The transport numbers of the ions of solid solutions of the system under investigation have been measured. Values less than 0.01 were obtained for the transport number of the cations. The values found experimentally for the anion transport numbers lie in the range 0.01-0.14. These results have been discussed in the light of the possibilities of using the weight method for measurements of transport numbers of ions of oxide systems.

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